# Three-dimensional silica-gold core-shell photonic crystal: linear reflection and ultrafast non-linear optical properties

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## ABSTRACT

In this paper we analyze linear and ultrafast non-linear properties of a three-dimensional photonic crystal composed of close-packed $SiO_2$/Au/$SiO_2$ core-shell colloidal particles. Strong coupling between incident light and surface plasmon of spherical gold microcavities appears as sharp features in observed reflectivity spectra in the visible. In a single layer of gold-shell particles, a highly directional diffraction pattern was observed with hexagonal symmetry. The non-linear dynamics of the reflectivity has been studied by femtosecond white-light pump-probe experiments. Abrupt changes limited by the instrumental time resolution, were observed in time-resolved reflection spectra while the signal recovers in about 10 ps. Ultrafast changes in reflectivity reach values as high as 20%. The results are compared with theory.

**Keywords**: photonic crystal, gold nanoshell, metallo-dielectric particles, plasmon, ultrafast dynamics, non-linear optics, core-shell colloidal particles, pump-probe.

## 1. INTRODUCTION

Progress in the fabrication of compound nanostructures that possess a spatial periodicity explains the rapid growth and interest in research on photonic crystals. This interest was initiated by the challenging idea to control the spontaneous emission of atoms or recombination in semiconductors.[1,2] However, photonic crystals are also relevant for various future applications ranging from telecommunication data processing to the realization of ultrafast switches and optical computers. In order to achieve full control over light flow in a photonic crystal, one needs to realize structures with a full photonic band gap – a spectral range, in which light cannot propagate in any direction. A photonic band gap can be created in a three-dimensional (3D) photonic crystal, which possesses 3D periodicity in the dielectric constant on the scale of the wavelength of light. Such crystals were fabricated for the first time by Blanco and co-workers[3] from a monodisperse suspension of colloidal microspheres that self-assemble into a 3D matrix with long-range periodicity. However, high-quality ordering is not sufficient to form a band gap. The additional requirement is to reach a sufficiently high refractive index contrast between the host and dielectric spheres. For example, the required refractive index contrast for close-packed face-centered-cubic (fcc) lattice of spheres should exceed 2.8 (Refs. 4 and 5). The most commonly used way to increase the refractive index contrast above the threshold is infiltrating the voids of the photonic crystal with semiconductors. The contrast may be increased further by etching out dielectric spheres.[3] However, even for such an inverted photonic crystal, the required refractive index contrast limits the material choice to highly refractive semiconductors, which are unfortunately opaque in the visible. Metallo-dielectric photonic crystals, however, are very attractive materials in this context because of their high refractive index. It was predicted that a large photonic band gap in the visible may open up in metallo-dielectric photonic crystals.[6] Further, metallo-dielectric photonic crystals turn out to be interesting objects from the point of view of fundamental optics.

In fact, the first and very well known and widely utilized periodic metallic structures are metallic gratings.[7] In 1902, Wood discovered anomalous sharp minima and maxima in the reflection spectra of metallic gratings.[8] Since that discovery, it took about 60 years to complete a theory that could account for all observed phenomena.[9] Roughly speaking, the anomalies can be traced back to two resonances: (i) one in which the diffraction orders graze the surface of the grating (proposed by Rayleigh)[10] and (ii) the plasmon resonance. These resonances may even interfere with each

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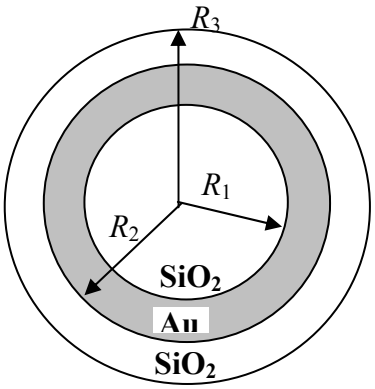


Fig. 1. Silica-core gold-shell particle with silica outer shell

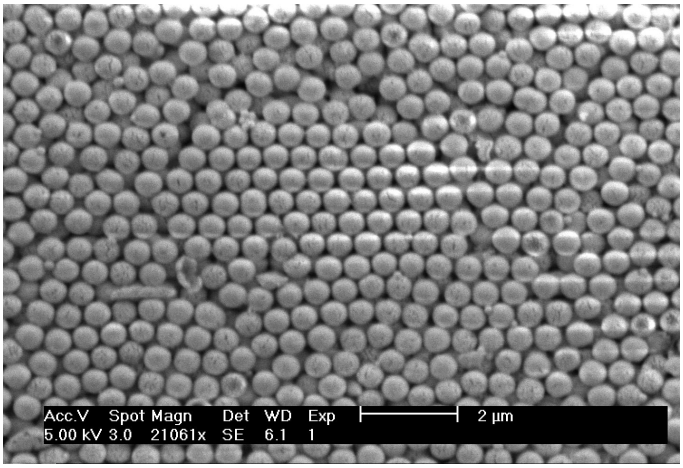


Fig. 2. SEM image of the fcc gold-shell photonic crystal on silicon substrate

other and produce a Fano-like profile of the reflectivity spectrum.[11,12] In the end of the twentieth century the interest in the metallic gratings was renewed by the work of Ebbesen and co-workers[13] who discovered unexpectedly high transmission through the array of sub-wavelength holes in a metal film, one order of magnitude higher than predicted by a standard aperture theory. This phenomenon was explained as follows: the incoming light excites the surface plasmons on the front side of the perforated film.[14] The excited plasmons transfer the energy via the holes to the other side of the film and, subsequently, radiate light into free space.

A related fascinating phenomenon takes place when light is transmitted through a suitably corrugated metal film having one single aperture of a size much smaller than the wavelength of light. Standard diffraction theory prescribes that light emerging from a sub-wavelength hole should be diffracted equally intense in all directions. However, Lezec with co-workers[15] demonstrated that the outcoming beam from a hole in a corrugated film can be very directional. The explanation of this phenomenon was found in the coupling of the plasmonic resonance with the corrugation at the rear surface of the film. The direction and the width of the outcoming beam can be controlled by the geometry of the structure and the incident wavelength. Very recently, Kramper and co-workers[16] showed both theoretically and experimentally, that a highly directional beam can be coupled out from a sub-wavelength waveguide even in a dielectric photonic crystal, demonstrating that these effects are not restricted to metallo-dielectric structures.

In this paper we study the linear and nonlinear optical properties of 3D photonic crystals composed of gold-shell spheres covered with a silica outer layer. In contrast to the case of a metallic film, this crystal does not support a propagating plasmon-polariton, because the gold shells are not touching. Instead, light can only excite discrete surface plasmon resonances, which result in the interplay between external and internal plasmonic resonances of single particles, accounted by the Mie theory.[17] Our studies were stimulated by calculations, which show that such a structure possesses a complete photonic band gap in the infrared. Here, however, in order to establish the physics of different resonance modes in our photonic crystal, we confine ourselves to optical properties in the visible range where surface plasmon resonances are expected to coexist with diffraction resonances of the periodic lattice. We examine both the reflection and the angular distribution of the diffracted light from the photonic crystal. In addition, we demonstrate ultrafast optical switching of the reflection induced by exciting the sample by a femtosecond 800-nm pulse.

This paper is organized as follows: In Sec. 2, we describe the sample parameters and experimental setup. In Sec. 3, we present the experimental results and in Sec. 4 the calculations. In Sec. 5 we discuss the results, and in Sec. 6 we summarize and conclude.

## 2. SAMPLE AND EXPERIMENTAL SETUP

### 2.1. Sample

Our sample consists of close-packed metallo-dielectric particles, forming a photonic crystal. Each particle has a silica core with a radius of 228 nm covered by a gold shell and capped with a silica outer shell with thicknesses of 38 nm and 10 nm, respectively, as shown in Fig. 1.

The detailed fabrication method of our sample is described elsewhere,[18] and is repeated briefly here. The metallic-dielectric spheres were synthesized in a multistep reaction. First, spherical silica particles of 228 nm radius were grown in a stepwise seeded Stöber growth process. In the second step, gold nanoclusters of 1-2 nm in diameter were attached to the silica spheres. Subsequently, these precursor spheres were put in a $HAuCl_4/K_2CO_3$ solution. Addition of hydroxylamine to this solution results in reductive growth and coalescence of the small gold clusters and the formation of a closed thin gold shell. Finally, capping the colloidal particles with an outer silica layer was achieved by surface functionalization with polyvinylpyrrolidone and subsequent growth by a Stöber like process.[19]

Since the silica outer shell reduces the van-der-Waals interparticle forces, the particles can be ordered in a periodic structure. Finally, a droplet of an ethanol solution containing the silica coated gold-shell colloidal particles was dried on a silicon waver to produce a close-packed array of the particles. Depending on the sample point, the thickness of the obtained photonic crystal appeared to vary from one monolayer to tens of monolayers. The scanning electron microscope (SEM) picture of a highly ordered part of the sample is shown in Fig. 2. We assume that our sample has an fcc structure.

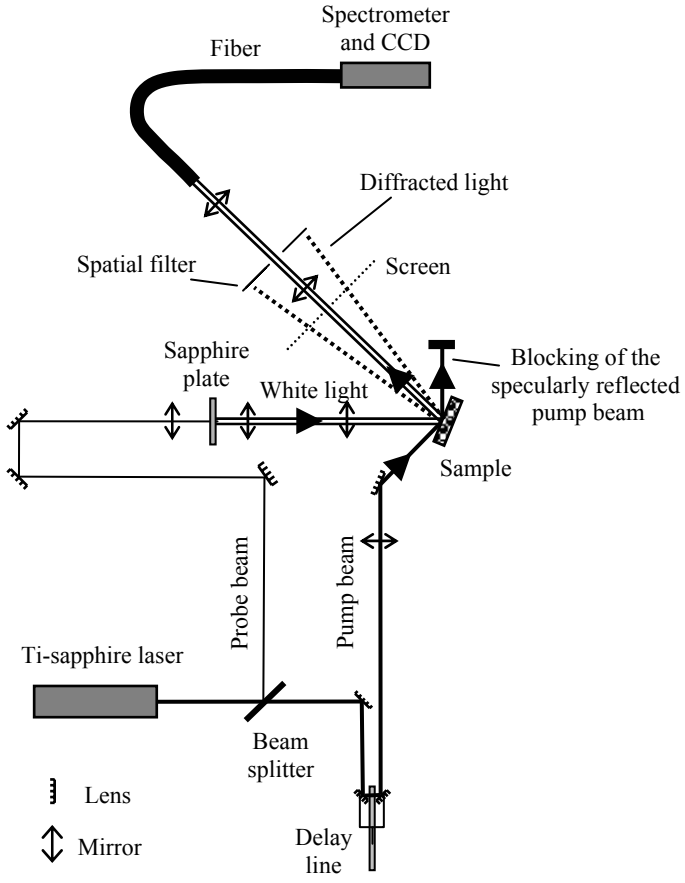


Fig. 3. Experimental setup.

### 2.2. Experimental setup

All experiments were carried out at room temperature. Stationary reflection spectra were obtained using a white light source generated on a sapphire plate as described below. The white light was directed at an angle θ to the [1 1 1] direction of the photonic crystal and focused onto a 25-μm spot at the sample surface. The reflected probe light was picked up by a lens, passed via a spatial filter, and focused onto the entrance of an optical fiber (Fig. 3). This fiber transferred the reflected light to the entrance slit of a spectrometer. The spectrum was detected by a charge-coupled device (CCD) controlled by a computer. In order to obtain the absolute value of the reflectivity from the photonic crystal, we used the part of the sample, which happens not to be covered by gold-shell particles and the well known reflectivity spectra of bulk silicon. The angle distribution of the reflected and diffracted light can be displayed on a screen inserted in front of the spatial filter (Fig. 3).

The ultrafast response of the photonic crystal was examined by a conventional pump-probe setup (Fig. 3). The photonic crystal was excited by an intense optical 120-fs pump pulse extracted from an amplified femtosecond 800-nm Ti-sapphire laser operated at 1 kHz. The pump pulse was focused onto a 400-μm spot at

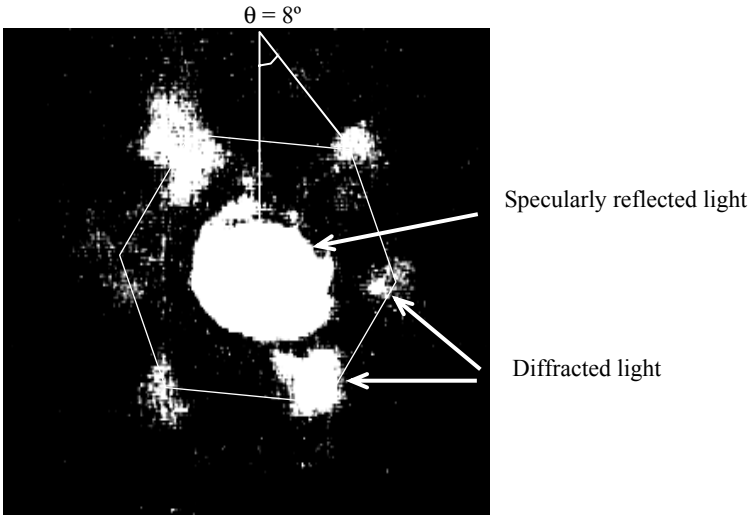


Fig. 4. Diffraction pattern from one layer of gold-shell particles on the silicon substrate. The angle between the propagation direction of the specularly reflected beam and the diffraction maxima is θ = 8°.

the sample surface resulting in a surface energy density of ~ 0.5 mJ/cm$^2$. The optical pulse excites electrons in the gold shell thus changing its complex dielectric constant and modifies the reflection properties of the photonic crystal. In order to avoid irreversible changes of the sample, the power density used in the experiment was kept well below the melting threshold. The induced changes in the reflectance spectrum were monitored by a weak ultrafast probe pulse of white light continuum generated in a sapphire plate, which was excited by the same Ti-sapphire laser. Further, in order to reject residual 800-nm light, the white light was passed through an optical filter. The resulting probe pulse was focused onto a 25-μm spot at the sample surface within the area of the pump. The intensity of the reflected probe light was detected in the same way as in case of the stationary experiments (see above). An optical delay line controls the delay between pump and probe pulses.

## 3. EXPERIMENTAL RESULTS

### 3.1 Linear optical properties

The linear optical properties of our photonic crystal turn out to depend on the number of layers of the gold-shell spheres on the substrate. However, as will be shown later, there are some general properties, that are found for any number of layers of the photonic crystal. Therefore, we describe the linear properties of a single layer of gold-shell particles first and subsequently will stress the differences that appear when more layers are present in the fcc-ordered photonic structure.

#### 3.1.1. Reflection from a single hexagonal layer of gold-shell particles.

A single layer of close-packed gold-shell particles is expected to be semitransparent for visible light. As a result, the main part of the reflected intensity should be due to specularly reflected light from the silicon substrate that manages to leak through the layer of particles. In addition to this, the reflection should have another contribution, i.e. due to diffraction on the periodic structure of ordered gold-shells. Figure 4 demonstrates the diffracted light intensity incident on a screen placed near the sample (the position of the screen is schematically shown on Fig. 2). Here, the central spot corresponds to the specularly reflected light. The specularly reflected beam propagates in a cone, which is limited by the aperture of the incident white light. The angular distribution of the diffraction pattern is strongly inhomogeneous and peaks roughly at the apexes of a hexagon. Surprisingly, the angle between the propagation direction of the specular

beam and the diffracted ones amounts to only $\theta \approx 8^{o}$. This small angle cannot be explained in terms of single particle scattering, nor by simple diffraction on a close-packed plain or fcc structure. The spectra of the diffracted and specular signals are shown in Fig. 5 by dotted and solid lines, respectively. The specular reflection (Fig. 5, solid line) peaks at 700 nm and has no spectral future in the green range of the spectrum (550 – 600 nm). However, the spectrum of the diffracted light (Fig. 5, dotted line) peaks at 570 nm and does not exhibit a maximum at 700 nm.

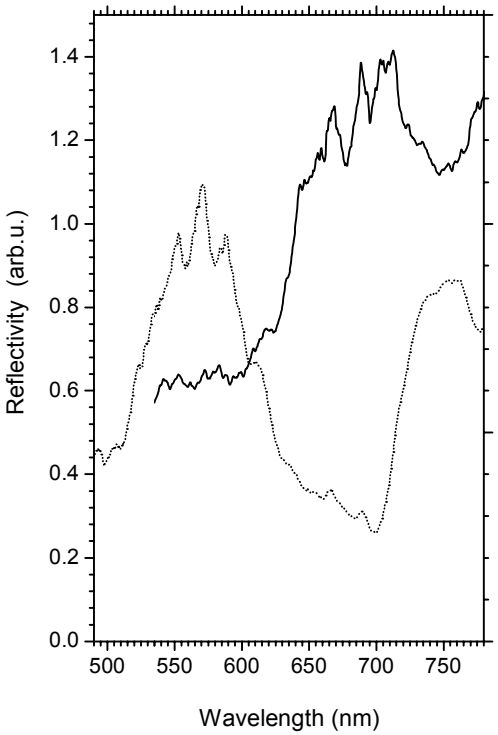


Fig. 5. Linear reflection spectra of the specularly reflected (solid line) and diffracted light (dotted line), respectively, from one layer of gold-shell particles on a silicon substrate.

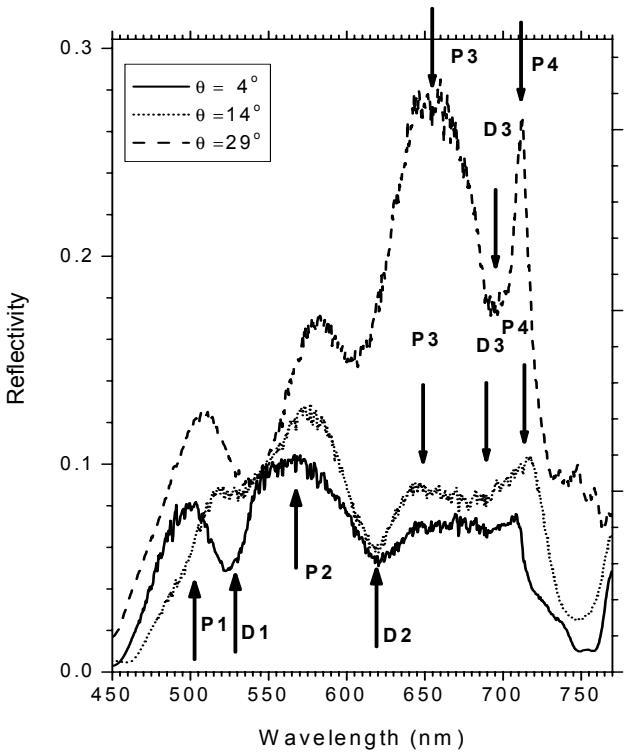


Fig. 6. Reflection spectra from thick (>5 layers) gold-shell photonic crystal at different angles of incidence, θ.

### 3.1.2. Reflection from a multi-layer gold-shell photonic crystal

Let us now describe the optical properties of more than one layer of ordered gold-shell particles that are stacked in a close-packed fcc matrix. In a sufficiently thick region of the crystal, the contribution from the reflection from the substrate vanishes. Moreover, the hexagonal diffraction pattern (Fig. 4) disappeared completely and only one beam was observed. This beam must originate from the reflection from the photonic structure, turns out to propagate in a narrow cone that is, however, slightly wider than the incident probe beam. Figure 6 shows the linear spectra of the reflected light at some selected angles of incidence. The spectra have a rather complicated structure consisting of peaks at 500, 570, 650, and 700 nm that denoted as P1, P2, P3, and P4, respectively, and dips at 530, 615, and 680 nm, denoted as D1, D2, and D2, respectively. The exact position of the maxima and minima slightly depends on the incident angle but was observed to be constant over the sample. We note that positions of P2 and P4 coincide with the single-layer reflection maxima of the diffracted and specular beams, respectively (Fig. 5).

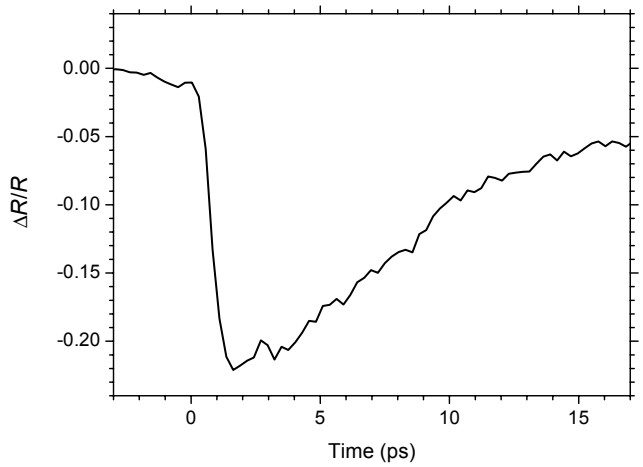


Fig. 7. Transient differential reflectivity from thick gold-shell photonic crystal measured at 650 nm after 0.5-mJ/cm$^2$ pump excitation at 800 nm.

### 3.2. Ultrafast response

In order to examine the ultrafast non-linear response of the gold-shell photonic crystal, we performed pump-probe experiment as described in Sec. 2.2. Figure 7 demonstrates the transient differential reflectivity, $\Delta R / R$, measured at 650 nm. The 800-nm optical excitation of the electrons in gold with the power density of about 0.5 mJ/cm$^2$ induces a rapid and large change in the dielectric constant. Following the pump excitation, the reflectivity of the photonic crystal rapidly decreases and reaches a value of $\Delta R / R = -0.22$. The subsequent return to equilibrium goes exponentially with a time constant of about 10 ps.

## 4. THEORY

The reflection, transmission, and absorption spectra were calculated using a photonic variant of the layer Korringa-Kohn-Rostocker (LKR) method (see, for instance Ref. 20). For the calculation we used the refractive index of silica $n(\mathrm{SiO}_2) = 1.45$ and a wavelength-dependent dielectric constant of gold.[21] We stress that the calculation uses no fitting parameters. Figure 8 shows the calculated reflection (solid line), transmission (dotted line), and absorption (dashed line) spectra of a single layer of the studied close-packed gold-shell particles at $\theta = 0$ angle of incidence. The calculated reflection spectra are in reasonable agreement with the experimentally observed ones (Fig. 6, solid line). This is remarkable because the calculation accounts only for a single layer, while the measurements were from the multilayer structure. The maxima P1, P2, P3, and P4 and minima D1, D2, and D3 of the measured spectrum are successfully reproduced in the calculation. The absorption spectrum peaks at 545 and 660 nm, which corresponds to dipole and quadrupole plasmon resonances, respectively.

## 5. DISCUSSION

The optical properties of the gold-shell photonic crystal are governed by two types of resonance: the external and internal surface plasmons of the gold shell (Mie resonances) and the resonant scattering on the periodic array of particles. The individual contributions of these resonances can be separated by examining the angle dependence of the reflection. In case, a resonance is associated with a plasmon resonance of an isolated particle with spherical symmetry, the spectral position of the resonance is angle independent. In case the resonance is associated with the ordering of the particles we do expect to observe an angle dependence. The observed maxima (P1-P4) and minima (D1-D3) in reflection (Fig. 6) spectrum can be classified into two groups: The first group, P1, D1, and P2, has maxima and minima that depend on the angle of incidence. Therefore, their properties must be associated with a periodic arrangement of the

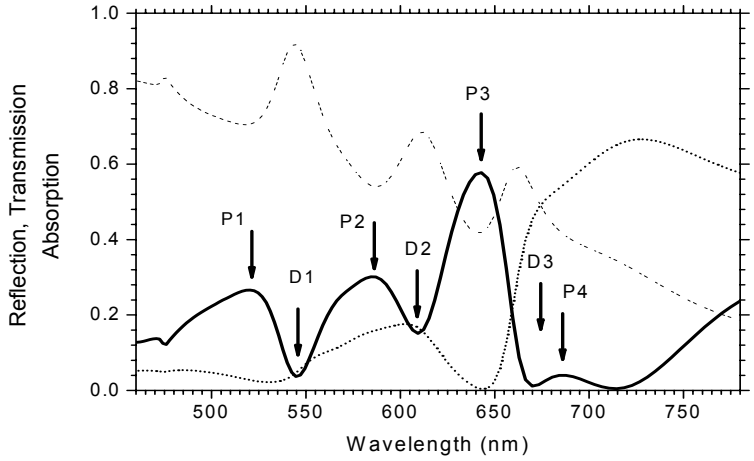


Fig. 8. Calculated reflection (solid line), transmission (dotted line), and absorption (dashed line) spectra of a single close-pack hexagonal layer of the gold-shell particles.

gold-shells. The second group, D2, D3, P3, and P4, has no angular dependence and, therefore, can be attributed to the plasmon modes. The calculations (Fig. 8) show that the minima in reflection spectrum, D2 and D3, coincide with the absorption and transmission maxima. Therefore, we believe that these spectral features are due to plasmonic modes excited in the crystal. In these modes the local amplitude of the electromagnetic field is enhanced which tends to increase the absorption.

We note, that the position of the resonance at 545 nm is very close to the lattice parameter $2R_3 = 548$ nm, which may result in a strong interference and possibly lead to some interesting phenomena. In Figure 4 we demonstrate that the propagation direction of light with a wavelength ~ 570 nm, diffracted on a single layer of ordered gold-shell particles, deviates from the specularly reflected light by $\theta = 8^\circ$ and produces a hexagonal diffraction. Although, the origin of this phenomena is not fully understood we speculate that interference of the localized plasmon and surface modes takes place. Similar effects were discussed recently by Martín-Moreno and co-authors[14] in their theoretical study of light propagation through a corrugated metallic film. Although, in contrast to Martín-Moreno's work, in our sample all plasmon modes are localized, but excitation of the propagating surface modes on a photonic-crystal-air interface should still be possible. In this connection it is relevant to note that Kramper and co-workers recently demonstrated highly directional emission from a subwavelength waveguide in a dielectric photonic crystal.[16]

Plasmonic resonances also lead to ultrafast and rather strong non-linear properties in the gold-shell photonic crystal. Electrons excited by the optical pump pulse induce an absorption that quenches plasmon resonances that leads to an increase or decrease of the reflectivity depending on the wavelength selected. Time-resolved spectra demonstrate abrupt changes within the instrumental time resolution. The subsequent recovery is controlled by electron-phonon interactions and appears to be somewhat longer than in bulk gold.[22] This is reminiscent of the elongation of the recovery time observed previously in gold sulfide particles covered by a thin gold film.[23] The observed changes in our system can reach values as high as 20% and require an excitation power that is one order of magnitude smaller than needed in silicon[24] or vanadium dioxide photonic crystals.[25]

## 6. CONCLUSIONS

In this paper we examined reflection spectra of an fcc-ordered three-dimensional crystal composed of silica-gold core-shell colloidal particles. The observed linear spectra in the visible consist of several maxima that can be traced down to stop-bands. The linear optical properties of gold-shell photonic crystals are governed by plasmon resonances. The reflection spectra are in agreement with calculations. In addition, we found that a single layer of gold-shell particles

produces a highly directional hexagonal diffraction pattern. Time-resolved spectra demonstrate rapid changes directly following the arrival of the pump pulse. The recovery time was observed to be ~ 10 ps. The observed changes in the reflected intensity can reach values as high as 20% at moderate pump powers, 0.5 mJ/cm$^2$. Our studies may prove to be relevant for future applications, such as microplasmonic circuits, ultrafast all-optical switches, and optical computers.

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## REFERENCES

1. V. P. Bykov, "Spontaneous Emission in a Periodic Structure", *Sov. Phys. JETP* **35**, 269-273, 1972.
2. E. Yablonovitch, "Inhibited Spontaneous Emission in Solid State Physics and Electronics", *Phys. Rev. Lett.* **58**, 2059-2062, 1987.
3. A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, and H. M. van Driel, "Large scale synthesis of a silicon photonic crystal with a complete three-dimensional bandgap near 1.5 micrometres", *Nature* (London) **405**, 437-440, 2000.
4. H. S. Sözüer, J. W. Haus, and R. Inguva, "Photonic bands: Convergence problems with the plane-wave method", *Phys. Rev. B* **45**, 13962-13972, 1992.
5. R. Biswas, M. M. Sigalas, G. Subramania, and K.-M. Ho, "Photonic band gaps in colloidal systems", *Phys. Rev. B* **57**, 3701-3705, 1998.
6. A. Moroz, "Three-Dimensional Complete Photonic-Band-gap Structures in the Visible", *Phys. Rev. Lett.* **83**, 5274-5277, 1999.
7. H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer-Verlag, Berlin, 1988.
8. R. W. Wood, "On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum", *Philos. Mag.* **4**, 396-402, 1902.
9. A. Hessel and A. A. Oliner, "A new theory of Wood's anomalies on optical gratings", *Appl. Opt.* **4**, 1275-1297, 1965.
10. Lord Rayleigh, "On the dynamical theory of gratings", *Proc. Roy. Soc.* (London) **A79,** 399-416, 1907.
11. Fano, "Some Theoretical Consideration on Anomalous Diffraction Gratings", Phys. Rev. **50**, 573, 1936.
12. U. Fano, "The theory of anomalous diffraction gratings and of quasi-stationary waves on metallic surfaces (Sommerfeld's waves)", *J. Opt. Soc. Am.* **31,** 213–222, 1941.
13. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, "Extraordinary optical transmission through sub-wavelength hole arrays", *Nature* (London) **391**, 667-669, 1998.
14. L. Martín-Moreno, F. J. García-Vidal, H. J. Lezec, A. Degiron, and T.W. Ebbesen, "Theory of Highly Directional Emission from a Single Subwavelength Aperture Surrounded by Surface Corrugations", *Phys. Rev. Lett.* **90**, 167401, 2003.
15. H. J. Lezec, A. Degiron, E. Devaux, R. A. Linke, L. Martin-Moreno, F. J. Garcia-Vidal, and T. W. Ebbesen, "Beaming Light from a Subwavelength Aperture", *Science* **297**, 820-822, 2002.
16. P. Kramper, M. Agio, C. M. Soukoulis, A. Birner, F. Müller, R. B.Wehrspohn, U. Gösele, and V. Sandoghdar, "Highly Directional Emission from Photonic Crystal Waveguides of Subwavelength Width", *Phys. Rev. Lett.* **92**, 113903, 2004.
17. G. Mie, "Beitrâge zur optik truber Medien, speziell kolloidaler Metallosungen", *Ann. Phys.* **25**, 377–452, 1908.
18. C. Graf and A. van Blaaderen, "Metallodielectric Colloidal Core-Shell Particles for Photonic Applications", *Langmuir* **18**, 524-534, 2002.
19. C. Graf, D. L. J. Vossen, A. Imhof and A. van Blaaderen, "A General Method to Coat Colloidal Particles with Silica", *Langmuir* **19**, 6693-6700, 2003.
20. A. Moroz, "Metallo-dielectric diamond and zinc-blende photonic crystals", *Phys. Rev. B* **66**, 115109, 2002.

21. *Optical properties of metals*, edited by J. H. Weaver, C. Kafka, D. W. Lynch, and E. E. Koch, Karlsruhe, vol. 2, Fachinformationszentrum Energie, 1981.
22. C. Suárez, W. E. Bron, and T. Juhasz, "Dynamic and Transport of Electron Carriers in Thin Gold Film", *Phys. Rev. Lett.* **75**, 4536-4539, 1995.
23. R. D. Averitt, S. L. Westcott, and N. J. Halas, "Ultrafast electron dynamic in gold nanoshells", *Phys. Rev B* **58**, R10203-R10206, 1998.
24. D. A. Mazurenko, A. V. Akimov, A. B. Pevtsov, D. A. Kurdyukov, V. G. Golubev, and J. I. Dijkhuis, "Ultrafast all-optical switching in a three-dimensional photonic crystal", *J. Lumin.* **108**, 163-166, 2004.
25. D. A. Mazurenko, R. Kerst, J. I. Dijkhuis, A. V. Akimov, V. G. Golubev, A. A. Kaplyanskii, D. A. Kurdyukov, A. B. Pevtsov, "Subpicosecond shifting of a photonic band gap in a three-dimensional photonic crystal" (in press).